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# Epitaxial Growth of Magnetic Nickel Nanodots by Pulsed Laser Deposition

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## ABSTRACT

Epitaxial nickel magnetic nanodots were obtained by pulsed laser deposition (PLD) technique on Si (100) substrate using epitaxial TiN film as the template. Characterization methods include: high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM) Z-contrast imaging, selected area electron diffraction (SAD), and X-ray diffraction (XRD) techniques. The results showed that as long as no coalescence between neighboring dots occurred, the dots are all single crystal. The predominant orientation relationship observed is Ni (100) // TiN (100) // Si (100), the so-called "cube-on-cube" orientation relationship. Other rotational orientation relationships, where the nickel crystal rotates an angle with respect to TiN (011) directions, were also observed. The dots are in faceted island shapes, bounded by (111) and (001) facets. The actual size of dots varies from a few nanometers to tens of nanometers, depending on the deposition time and temperature. The shape of a certain dot was found to be closely related to its epitaxial orientation. Effects of deposition temperature and template crystalline quality were studied. It was found that deposition temperature in a certain range does not have much influence on the epitaxial orientation of dots, while the crystalline quality of titanium nitride (the underlying template) is primarily responsible for the orientation variation. At the optimum condition, samples with a large fraction of cube-on-cube orientated nickel dots could be obtained in a rather wide temperature range (up to 250 °C), as evidenced by the strong reflections from both SAD and XRD. Samples containing more than one layer of nickel and titanium nitride matrix were also studied. The results showed that the degree of orientation perfection could be greatly improved by decreasing the size of dots.

## INTRODUCTION

Nanomagnetic materials have drawn significant attention in recent years due to their dramatically improved physical properties, which are critical for enhancing the magnetic device performance [1-4]. The potential applications in ultrahigh density information storage make the effective fabrication of magnetic nanodots with controlled properties highly desirable. Magnetic properties of the nanomagnetic materials are closely related to the magnetic anisotropy of the material, which depends not only on the size, shape and strain state of the particles, but also on their crystal structure and orientation. So far, however, most studies in this area have been focused on the dependence of magnetic properties on the particle size and separation.

In our previous research [5,7], magnetic measurements were conducted on the samples containing nickel nanodots embedded in an epitaxial titanium nitride matrix, and the results were compared with that of the nickel nanodots of similar size embedded in amorphous alumina matrix. It was found that although not all nickel dots are oriented in the same way (both cube-on-cube and rotational orientation were observed) and the crystalline quality of titanium nitride used as the template deteriorated due to the inclusion of nickel dots, still a considerably higher

blocking temperature and coercivity, compared to that of completely randomly oriented nickel nanodots grown on amorphous alumina, were observed. The higher value of coercivity is possibly associated with the stronger tendency of crystallographically oriented particles to retain their magnetic moments in the presence of a reverse magnetic field.

The purpose of this study is to investigate the effect of deposition temperature and crystalline quality of the titanium nitride template on the nickel nanodots orientation, so that samples with highly oriented nickel nanodots could be obtained. In addition, since our magnetic measurements were conducted on samples containing more than one nickel and titanium matrix layers for stronger signal, investigations on the orientation perfection of nickel nanodots as a function of the number of the layers are also needed.

## EXPERIMENTAL DETAILS

Ni nanodots and the TiN template layers were deposited by ablating a pure nickel target and a hot pressed titanium nitride target in a pulsed laser deposition (PLD) system, respectively. Si (100) wafers were used as the substrate since both titanium nitride and nickel have the face-centered cubic structure and titanium nitride has been reported to be epitaxially grown on silicon (100) substrates by domain matching [6]. The substrate cleaning and details of deposition process have been described elsewhere [5,7]. For studying the effect of deposition temperature on the nickel orientation, the deposition temperature for nickel was varied in the range of 400 °C to 650 °C while that for titanium nitride was kept at 600 °C [6], so that the contributions from the variation of template crystalline quality due to the deposition temperature change could be excluded. Multi-layer samples containing two and three layers of nickel were prepared by alternatively ablating titanium nitride and nickel targets.

Dots morphology, size and orientation, as well as the crystalline quality information of the template (matrix in the case of multi-layer samples) were studied by conventional (TEM), high-resolution transmission electron microscopy (HRTEM), and scanning transmission electron microscopy (STEM) Z-contrast imaging (TOPCON 002B and JEOL 2010F). X-ray diffraction (XRD) was used to determine the crystalline quality for a larger area of the sample. Both cross-section and plan view samples for TEM study were prepared by mechanical polishing, followed by ion milling.

## RESULTS AND DISCUSSION

### One-layer sample: dots shape, size, orientation and their temperature dependence

Although in our previous study [5,7], a significant fraction of nickel dots were found to grow via rotational orientation, this time, under all deposition temperatures (400 °C, 500 °C, 600 °C and 650 °C), we have been able to obtain samples with cube-on-cube being the nickel predominant epitaxial orientation. Shown in Figure 1 (b) and (c) are typical cross-sectional and plan-view electron diffraction patterns taken from an area containing silicon, titanium nitride and nickel. The alignment of diffraction spots of Si, TiN and Ni clearly indicates the predominant cube-on-cube epitaxial orientation relationship for both TiN and Ni, described by Ni(100) // TiN(100) // Si(100). In the plan-view pattern, sets of double-diffraction spots also appeared due

to the overlapping of silicon, titanium nitride and nickel. High-resolution image (Figure 1 (a)) confirmed this orientation relationship and showed that the epitaxial growth of Ni dots on TiN template is also by domain matching [6], which is a common case for heteroepitaxy with large lattice mismatch between the substrate and the film. From Si [011] zone axis low-magnification image (Figure 1 (d)), we can see that uniformly separated nickel dots are of faceted island shapes, and the common morphology is trapezoidal, corresponding to cube-on-cube oriented growth as found in previous research (dots grown via rotational orientation are in triangular morphology [5,7]). The actual size of dots varies from a few nanometers to tens of nanometers, depending on the deposition time and temperature. The size distribution of individual dots is relatively narrow (those in larger lateral size mostly resulted from coalescence of two neighboring dots). The interface between TiN and Ni shown in the Z-contrast image (Figure 1 (e)) is quite sharp, which means no significant interfacial reaction occurred since the intensity of Z-contrast image is proportional to the square of the atomic number.

The facets of nickel islands have also been studied from the high resolution images combined with low magnification images. It was found that the dots grown via cube-on-cube orientation relationship are bounded by (001) facets at the top and (111) facets at sides, with the two (111) planes forming an angle of 70.52° with each other. The dots grown via rotational orientation relationship were also bounded by (111) facets, but the angle formed by two planes is 109.48°, and there is no flat-top observed [8]. In the crystallographic point of view, the latter case is actually a result of the nickel nanocrystal rotating along the template <011> direction (also the zone axis of TEM image) about an angle close to 90° [8]. The fact that in both cases (111) facets play a prominent role in surface morphology can be explained in the terms of surface energy anisotropies. L. Vitos and coworkers[9] calculated the surface energy for 60 metals by full charge density (FCD) in generalized gradient approximation (GGA) method. Their result showed that for nickel, (111) surface has the smallest surface energies among low index surfaces[9]. For transition metals, the main contribution to the surface energies comes from the dangling bonds at the semi-infinite surface. The number of such bonds increases as the surface becomes more open[9].

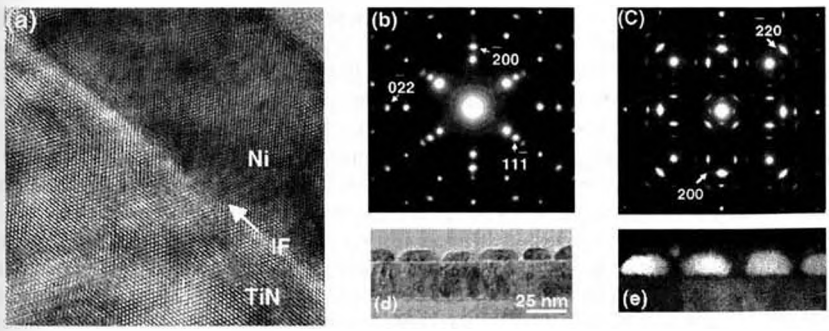


**Figure 1.** (a) Si [011] zone axis HRTEM image of a cube-on-cube oriented nickel island; SAD pattern taken from an area containing silicon substrate, titanium nitride template and nickel dots for (b) cross-sectional with Si [011] as zone axis and (c) plan-view with Si [001] as zone axis (sets of double diffraction spots are clearly seen); Image of an array of trapezoidal-shaped nickel dots is shown in (d) low-magnification TEM; (e) STEM Z-contrast image.

As mentioned earlier, in the 400 °C to 650 °C temperature range, the cube-on-cube nickel epitaxy is predominant, as evidenced by electron diffraction and x-ray diffraction patterns. This suggests that the thermal energy of nickel atoms gained from the substrate heating is not the determining factor for the orientation of dots during epitaxial growth. However, deposition temperature does have influence on the final shape of the dots. While the trapezoidal morphology is retained, the ratio of height to lateral size is decreased with decreases in deposition temperatures, which could be explained by the fact that 3-dimensional growth is more favorable at higher temperatures.

**Multi-layer sample: orientation perfection and its layer number dependence**

Shown in Figure 2 (a) and (b) are the low-magnification image and cross-sectional electron diffraction pattern of a two-layer sample deposited at 600 °C. The diffraction spots contributing from cube-on-cube oriented nickel dots are still clearly seen. Compared with that of the one-layer samples, the titanium nitride diffraction shows obvious signal of texturing (misoriented by an angle, mostly of a few degrees). Besides, some spots corresponding to rotated nickel are also visible. The strong diffraction of cube-on-cube oriented nickel mostly comes from the dots in the first layer, where the template is undisturbed and crystalline quality is good. This was supported by the observation that the morphologies of the first-layer of nickel are mostly trapezoidal, an evidence of cube-cube growth. Also, it is easy to understand the texturing of titanium nitride since the orientation perfection of titanium nitride template would deteriorate due to the repeated lattice match interruption, as more layers of the nickel dots are included. HRTEM study of second-layer dots shows that although there is still a fraction of dots grown via cube-on-cube orientation, a number of triangular-shaped dots grown via rotational orientation start to form, which is supported by the x-ray diffraction pattern (Figure 3), where the Ni (220) peak appeared along with TiN (200) and Si (400) peaks.

In order to improve the orientation perfection of template titanium nitride and therefore nickel nanodots, we decreased the deposition time of nickel from 40 seconds (used in two-layer sample) to 20 seconds. Figure 2 (c) is the diffraction pattern from the cross-sectional sample containing three layers of nickel and titanium nitride. It is easily seen that the texturing of titanium nitride has been greatly suppressed. The cube-on-cube nickel spots are weak due to the significant decrease in the amount of nickel, but still visible. Besides, double diffraction spots from titanium nitride and nickel also appeared since the first two layers of nickel are embedded in a titanium nitride matrix. The fact that we can still get a moderate template crystalline quality for multi-layer samples is partially due to the lateral epitaxy of titanium nitride, which originates from the titanium nitride areas uncovered by nickel dots in the previous layer. Fast Fourier Transform (FFT) (not shown here) from the high-resolution images of embedded first-layer nickel dots clearly showed double diffraction spots, identifying the lateral epitaxy of nickel.

In film heteroepitaxial growth, there are several factors that will affect the epitaxial orientation, such as lattice mismatch, interfacial inter-atomic bonding[10], and the atomic mobility determined by both the thermal energy of the atoms and the substrate surface local roughness (topographical features of the substrate). In all nickel rotational orientation growth cases we observed, two sets of (111) planes have tilted themselves to a smaller inclination angle with respect to the template surface, compared to that of the cube-on-cube case, and as a result the lattice mismatch has been considerably reduced. However, the predominant orientation of

nickel observed is cube-on-cube. Therefore, lattice mismatch could not be the determining factor in this case. The fact that the rotational epitaxial growth tends to occur in the samples where the silicon substrate cleaning, for some reason, was not good, or in the multi-layer samples, suggests that the local structure in the template plays an important role here. The local atomic structure of template could directly affect the interfacial inter-atomic bond length, and therefore the bond energy[10]. The topographical features could also influence the nucleation site and the mobility of the adatoms. Further investigation of the interfaces is necessary to obtain a detailed mechanism.

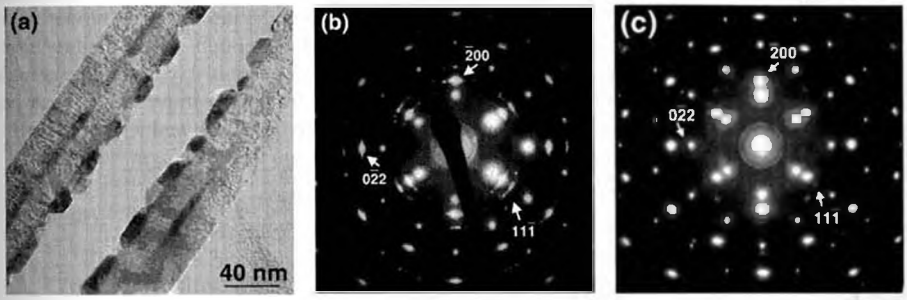


**Figure 2.** (a) Low-magnification image of a sample with two layers of nickel dots, note that although there is still strong tendency for nickel cube-on-cube growth, the triangular-shaped dots start to formed on the second layer; Cross-sectional selected area electron diffraction along Si [011] zone axis of samples containing (b) two layers of nickel dots; and (b) three layers of nickel dots. The texturing of TiN and Ni shown in (b) is considerably suppressed in (c).

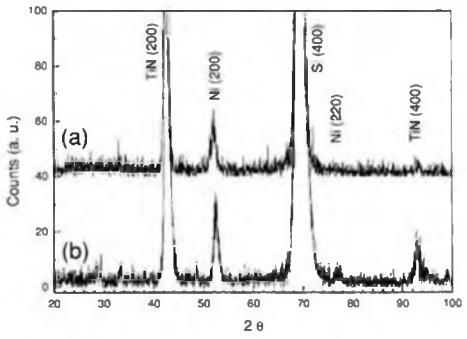


Figure 3. X-ray diffraction patterns of samples containing (a) one-layer and (b) two-layer nickel nanodots grown at 600 °C. For the two-layer sample, (220) reflection from Ni dots grown via rotational orientation is also seen.

## CONCLUSIONS

In summary, we have deposited epitaxial nickel magnetic nanodots by pulsed laser deposition technique on Si (100) substrates using epitaxial TiN films as the template. The predominant epitaxial relationship was determined by both electron diffraction and x-ray diffraction to be cube-on-cube with Ni(001) // TiN(001) // Si(001). The dots are in faceted island shapes, bounded by (111) and (001) facets. The actual size of dots varies from a few nanometers to tens of nanometers, depending on the deposition time and temperature. Other rotational orientation relationships, where the nickel crystal rotates an angle with respect to TiN (011) directions, are also observed. Deposition temperature in a certain range does not have much influence on the epitaxial orientation of dots, but does affect the ratio of height to lateral size in the trapezoidal morphology, which cube-on-cube oriented nickel dots were found to adopt. By decreasing the size of nickel dots, the orientation perfection of multi-layer samples containing more than one nickel and titanium nitride matrix layers were greatly improved. The appearance of rotational oriented dots could not be explained by lattice mismatch and we suggests the template local structure, in terms of atomic configuration and topographical feature, is responsible for this rotational orientation.

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